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THE SOLUBILITY OF CALCIUM CARBONATE AND OF MAGNESIUM HYDROXIDE AND THE PRECIPITATION OF THESE SALTS WITH LIME WATER.

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THE problem of water softening is attaining such great importance that it seems advisable at this time to re-examine carefully the principles and chemical data involved, in order to render them as correct and trustworthy as possible. Prominent among the questions to be settled are the solubilities of normal calcium carbonate and of magnesium hydroxide.

SOLUBILITY OF NORMAL CALCIUM CARBONATE.

The values given for the solubility of calcium carbonate by the different authorities quoted in Comey's *Dictionary of Chemical Solubilities*[1] vary from 10 to 113 parts per million. About one-half of these authorities give values of more than 50 parts per million, but the high figures represent chiefly the results of early experiments, and are evidently erroneous. The figures which appear to be most reasonable may be divided into two groups, one placing the solubility between 20 and 36 parts per million, the other, between 10 and 16 parts per million.

TABLE I.

GROUP I.

Authority	Date	Temperature ° C.	Solubility in Parts per Million
Chevalet[2]	1869	..	34
Hoffman[3]	1865	..	34
Peligot[4]	....	..	20
Weltzien[5]	1865	..	36

GROUP II.

Authority	Date	Temperature ° C.	Solubility in Parts per Million
Bineau[6]	1857	..	16.0
Schlösing[7]	1872	16.0	13.1
Holleman[8]	1893	8.7	10.0
Holleman[8]	1893	23.8	12.5
Kohlrausch and Rose[9]	1893	18.0	13.0

Various methods were employed by the different investigators to secure these results, as indicated in the subjoined notes. Those who obtained values greater than 30 parts per million did not mention having taken any precaution against two of the greatest sources of error involved, namely, the influence of the CO_2 of the air, and the action of the solution of $CaCO_3$ upon the glass vessels. It seems significant that the figures of Bineau, who apparently first made allowance for these sources of error, and those of the modern experimenters, who followed his example, are all well under 20. The value most commonly accepted for the solubility of the normal calcium carbonate is 30 parts per million, although Kimberly, in a recent paper,[10] used 20 parts per million as the best value.

Several preliminary experiments to determine the solubility of normal calcium carbonate were conducted by one of us, in 1903. The pure salt was boiled with distilled water, free from CO_2, in flasks of Bohemian glass, and after standing for some days, protected from the CO_2 of the air, the resulting solution was filtered and titrated with N/50 acid. The results so obtained were 30.5 parts per million by one set of experiments, and 25 parts per million by another. During the following year these experiments were repeated, giving in one case 23 parts per million and in another 13.5 parts per million. The last value was obtained when a flask of Jena glass was substituted for the Bohemian glass flasks.

In order to determine the reason for these discrepancies and to obtain correct and concordant results, the following experiments were performed:

Two liter flasks of Jena glass were each fitted with a one-hole rubber stopper, through which projected a short piece of glass tubing, drawn to capillary dimensions at its upper end. Into each flask was put about 900 c.c. of distilled water, absolutely neutral in reaction to methyl orange, and lacmoid. The contents of the flasks were boiled for two hours, in order to drive off the last trace of CO_2 gas, and at the end of this time the stoppers were removed, and replaced, as quickly as possible, before any air could enter, by one-hole stoppers each bearing a U tube filled with beads, well moistened with fresh concentrated NaOH solution, the bend of the tube forming an effective seal. Flask 1 was cooled to 37° C. by allowing it to stand over night in an incubator adjusted to maintain that temperature, while Flask 2 was cooled to room temperature (21° C.). There was then quickly introduced into each flask 5 g. $CaCO_3$, prepared by thoroughly washing the best procurable chemically pure product with hot distilled water, and drying to constant weight at 100°–110° C. After stoppering with solid rubber stoppers, the flasks were kept, respectively, at the temperatures mentioned, and were frequently well shaken throughout the experiment, in order to render solution complete. At intervals of 24 hours portions were withdrawn, quickly filtered through paper, and 100 c.c. of the filtrate titrated with N/50 H_2SO_4, using phenolphthalein and methyl orange as indicators. The results are shown in the following table:

TABLE 2.

FLASK 1.

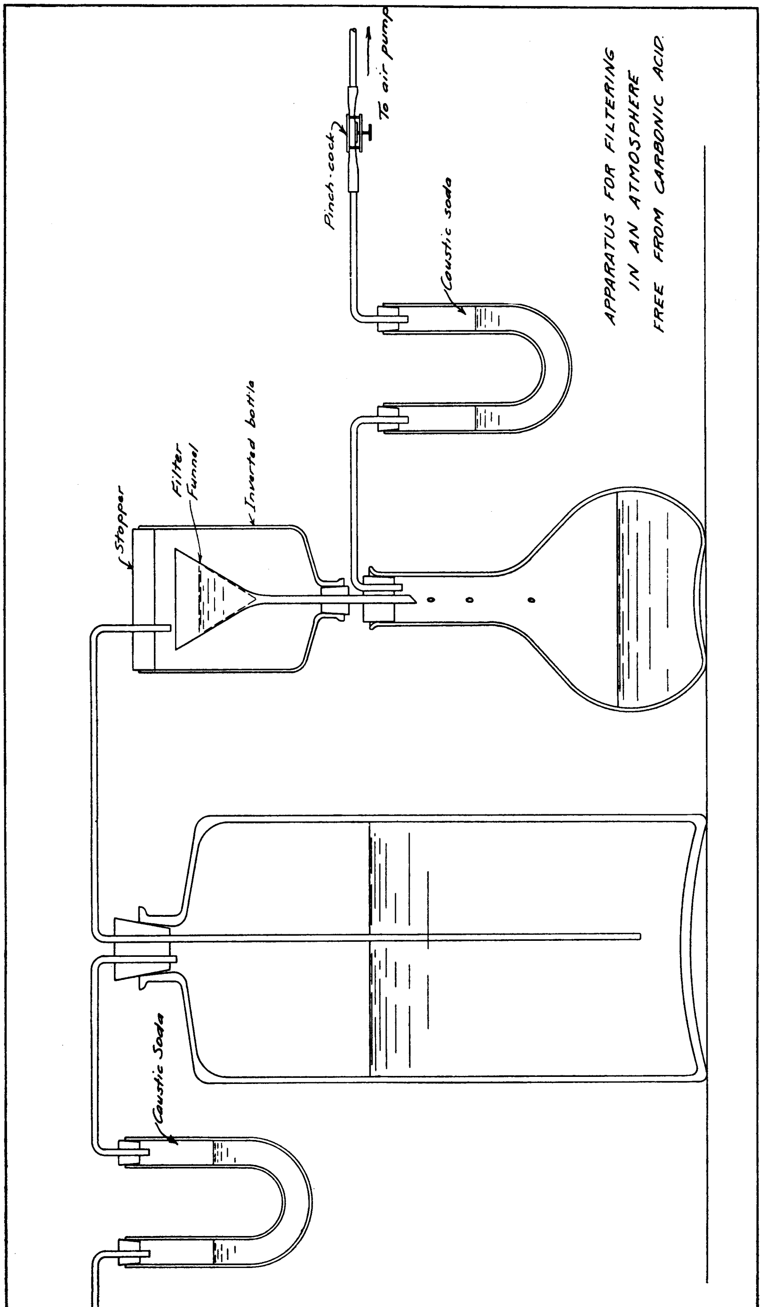
TIME	TEMPERATURE ° C.	ALKALINITY	
		Phenol-phthalein	With Methyl Orange
24 hours	37.5	...	15.0
53 "	"	7.0	15.0
77 "	"	6.5	14.5
FLASK 2.			
28 hours	23	6.5	14.0
53 "	22	6.0	13.0
76 "	20	6.5	13.0

The N/50 H_2SO_4 used in all this work was prepared from normal sulphuric acid, which was checked by titration against pure sodium carbonate, and by the gravimetric determination as barium sulphate. The dilution was done by means of a pipette and flask, which were calibrated against each other.

Another experiment, carried out in practically the same manner as those above described, at 20° C., gave 13 parts per million.

A value of 13 was also obtained by an experiment in which pure water, free from CO_2, was boiled, with an excess of chemically pure $CaCO_3$, for three hours in a flask of Jena glass, and allowed to stand with frequent agitation, protected from the CO_2 of the air as above described, for a period of four days.

The alkalinity of the solution of $CaCO_3$, using phenolphthalein as indicator, should be equal to one-half of the value obtained by using methyl orange as indicator. It was found, however, when the solution was filtered in the air, that enough CO_2 was dissolved to reduce the phenolphthalein figure. In order to overcome this difficulty, an apparatus was made to filter solutions out of contact with CO_2. (See diagram.) This apparatus, although accomplishing its object, consumed considerable time, as it was necessary, before attempting filtration, to remove from the apparatus every trace of CO_2 gas by aspiration. The method finally adopted for securing the $CaCO_3$ solution free from suspended particles, as well as CO_2, consisted in allowing all the $CaCO_3$ to settle, after which 100 c.c. of the clear



APPARATUS FOR FILTERING IN AN ATMOSPHERE FREE FROM CARBONIC ACID.

supernatant solution could be drawn off with a pipette attached to a filter pump by a rubber tube. In every case in which this was done, all error due to the presence of CO_2 in the air was avoided, and the phenolphthalein value was equal to just one-half the methyl orange value, as it should be. (See Table 2.)

In order to throw some light upon the high figures obtained in the preliminary work mentioned, experiments were conducted with flasks of Jena and Bohemian glass, in exactly the same manner as those last described, but omitting the addition of $CaCO_3$. The results of these blank tests are given in the following table:

TABLE 3.

TIME OF BOILING	TIME OF STANDING	ALKALINITY (PARTS PER MILLION)							
		Flask 1		Flask 2		Flask 3		Flask 4	
		P.*	M.†	P.	M.	P.	M.	P.	M.
1 hour......	0 days	..	1.0	..	..	0.5	2.0	..	..
2 hours.....	4 "	..	..	..	..	..	..	10.5	12.5
2 "	3 "	..	..	0.75	1.5	..	..	..	..
3 "	0 "	0	..	..	..	4.0	6.5	..	..
4½ "	0 "	0	1.5	..	..	5.5	9.5	..	..
4¾ "	5 "	0	2.5	..	..	7.0	10.0	..	..

*Phenolphthalein. †Methyl orange.

1 and 2 Jena glass flasks. 3 and 4 Bohemian glass flasks.

As the presence of small amounts of alkali in solution accelerates the action of water upon glass, and as the flasks used in the preliminary experiments were, with one exception, made of Bohemian glass, it can be readily seen why the figures first obtained were so high and variable. If, however, we subtract the average figure obtained in the blank experiments on Bohemian flasks, namely, 11.25, from the values obtained in the preliminary experiments, in which that kind of glass was used, we obtain values of 12 to 19 parts per million.

A better figure, however, is arrived at by subtracting from the results obtained in Jena flasks the corresponding blank, namely, 1.5, which gives us, in round numbers, 12 parts per million at 22° C., and 14 parts per million at 37.5° C.

The figures for the solubility of normal calcium carbonate, i. e., from 12 to 14 parts per million, were corroborated by other experiments described later, in which calcium bicarbonate solution was treated with lime water. The solubility of $CaCO_3$ in water is influenced by the presence of other substances. Salts of ammonia, for example, tend to render it more soluble, while other substances decrease the solubility. We found, for instance, that in water containing 500 parts per million of pure $CaSO_4$, the solubility of $CaCO_3$ was 4.5 parts per million at room temperature, while in water containing 1,000 parts per million $CaSO_4$, the solubility of $CaCO_3$ was 4.0 parts per million. The effect of the presence of various salts on the solubility of $CaCO_3$, on account of its importance, has been left for subsequent discussion in detail.

SOLUBILITY OF MAGNESIUM HYDROXIDE.

When magnesium carbonate is precipitated from aqueous solution with alkaline salts, the product is invariably basic, that is to say, the carbonate contains a certain amount of hydroxide. The exact composition of this precipitate varies according to conditions, temperature being a very important factor. The solubilities of normal magnesium carbonate or basic magnesium carbonate, therefore, cannot be definitely fixed. It is certain, however, that all modifications of basic magnesium carbonate are much more soluble than magnesium hydroxide, and in water softening, sufficient lime water is added to precipitate all the magnesium in the latter form, i. e., as MgO_2H_2.

The values for the solubility of MgO_2H_2 as given by most of the early experimenters, quoted by Comey,[1] are so high as to be obviously worthless. The most probable figures, as shown by Table 4, vary from 9 to 20 parts per million:

TABLE 4.

AUTHORITY	DATE	TEMPERATURE	SOLUBILITY OF MgO_2H_2	
			Parts per Million	Equivalent Alkalinity, i. e., as $CaCO_3$
Fresenius[11]......................	1847	"Ordinary" and 100° C.	18	31
Bineau[12]........................	1855	"Ordinary"	10–20	17–34
Kohlrausch and Rose[9]...........	1893	18° C.	9	16

In determining the solubility of this salt, the same method was employed as for $CaCO_3$. The best grade of MgO, freshly ignited in order to decompose any carbonate present, was used.

The results are shown in the following table:

TABLE 5.

TIME IN HOURS	TEMPERATURE	ALKALINITY IN TERMS OF $CaCO_3$	MAGNESIUM HYDROXIDE (PARTS PER MILLION)	
			Observed	Corrected for Blank
120	22° C.	23	13	12
144	"	23	13	12

Both experiments were conducted in flasks of Jena glass.

This method for MgO_2H_2 presents considerable difficulty. Magnesium hydroxide is a colloidal precipitate, which requires a long time to settle, and tends to pass through filter paper. Therefore the results may be somewhat in excess of the true value.

PRECIPITATION OF LIME AND MAGNESIA WITH LIME WATER.

Although $CaCO_3$ and $MgCO_3$ are with difficulty soluble in pure water, they dissolve readily in water containing CO_2 to the extent of about 1 g. per liter for $CaCO_3$, and 20 g. per liter for $MgCO_3$, at ordinary temperature and pressure. The state in which these salts exist in solution is not definitely established, but they may be represented respectively by the formulas $CaCO_3$, CO_2, H_2O, and $MgCO_3$, Co_2, H_2O. They are precipitated from solution by lime water according to the following equations:

$$CaCO_3, CO_2, H_2O + CaO_2H_2 = 2CaCO_3 + 2H_2O \quad \text{and}$$
$$MgCO_3, CO_2, H_2O + 2CaO_2H_2 = MgO_2H_2 + 2CaCO_3 + 2H_2O.$$

In order to corroborate the evidence already obtained as to the solubility of $CaCO_3$ and MgO_2H_2, and also to throw some light upon the course of the reactions which take place when bicarbonates of lime and magnesia are precipitated with lime water, the following experiments were undertaken.

The solutions used were prepared as follows:

Pure $CaCO_3$ was suspended in distilled water, and CO_2 gas passed in for some time. After the undissolved $CaCO_3$ had settled, the supernatant fluid was poured into a large evaporating dish, and allowed to stand over night, thus allowing the excess of free CO_2 to escape. The liquid was then filtered, giving a fairly strong solution of pure calcium bicarbonate, which could be diluted to any strength desired. Magnesium bicarbonate was prepared in a similar manner from the purest obtainable carbonate of magnesium.

Lime water was made in the usual manner, by shaking distilled water with an excess of freshly slaked lime and filtering the resulting solution. For some experiments a chemically pure lime was used, but the solution obtained from this differed in no appreciable respect, for this purpose, from that obtained with good commercial lime. The strength of these solutions was determined by titration with N/50 H_2SO_4, using phenolphthalein as indicator in the case of lime water, and methyl orange in the case of the bicarbonates. The precipitation experiments were performed as follows: The desired amount of bicarbonate solution was measured with as much accuracy as possible into a bottle of flint glass with a rubber stopper, and brought to the desired temperature. The volumes used varied from 1.8 to 3.5 liters, in bottles of 2 and 4 liters capacity, respectively. 100 c.c. was then quickly withdrawn, and the amount of free CO_2 determined by titration with carefully prepared N/22, Na_2CO_3 solution, using phenolphthalein as indicator. Then, the alkalinity and volume of the bicarbonate solution, the amount of free CO_2 gas, and the strength of the lime water being known, a simple calculation sufficed to determine the exact amount of lime water necessary to cause the desired reaction. After the addition of lime water the contents of the bottle were thoroughly mixed by shaking, and maintained at the desired temperature as long as necessary. The amount of calcium carbonate in solution was determined, when desired, by withdrawing a portion of the solution, filtering quikly through paper, and titrating with N/50 H_2SO_4 as usual.

PRECIPITATION OF CALCIUM CARBONATE.

In the experiments where calcium bicarbonate alone was used, the precipitate which first formed upon adding lime water was colloidal in character, but gradually changed, becoming crystalline in about 20 minutes. This change took place more quickly at higher temperatures than at low temperatures. At 38° C. it required only about 10 minutes, while at 9° C. it required nearly 30 minutes.

Three preliminary experiments with calcium bicarbonate, which were conducted at room temperature as described above, gave the results shown in Table 6. Just enough lime water was added to neutralize all the free CO_2 and precipitate all the calcium as carbonate.

TABLE 6.

Experiment Number	Time of Standing in Hours	Temperature	Parts per Million $CaCO_3$
I	1	22° C.	92
II	3.5	22	35
III	6	22	26

It will be noticed that the amount of $CaCO_3$ remaining in solution was inversely proportional to the time of standing, and it is evident, therefore, that the time element is of much importance in this reaction.

In order to investigate this question more thoroughly, another experiment, like those just described, was carried on at room temperature. Portions of the solution were withdrawn for analysis at intervals, until the amount of $CaCO_3$ remaining in solution had reached a minimum.

The results obtained are shown in Table 7.

TABLE 7.

Time in Hours	Temperature	$CaCO_3$ (Parts per Million)
0	....	180*
1	19° C.	70
3	20	60
6	20	43
24	22	22
50	22	18
74	19	17
122	20.5	14.5
218	20.5	15
720	20.5	17.5

*Calcium bicarbonate solution before addition of lime water.

In these, as in most of the experiments, the initial alkalinity of the water made no appreciable difference in the rapidity of the reaction after the solution had stood a few hours. In all cases, the results obtained by using phenolphthalein as indicator were one-half of those obtained with methyl orange; and this was found to be true at all stages of the reaction. The experiment recorded in Table 7 was repeated, and figures were obtained which practically checked those given.

The above experiment was then twice repeated, but in one case the solution was kept at a temperature of 2° C., and in the other case at a temperature of 35° C., the other conditions being the same as above. The results of these experiments are given in Tables 8 and 9.

TABLE 8.

Time in Hours	Temperature	Parts per Million of $CaCO_3$
0	1° C.	170*
1	2	313
4	2	59
6	2	49
24	2	28
52	2	18
77	2	17
173	2	15.5
312	2	15.5

*Before adding lime water.

TABLE 9.

Time in Hours	Temperature	Parts per Million of $CaCO_3$
0	35° C.	197*
0.25	35	43
0.75	35	29
5.75	35	24
28.0	35	18.5
54.0	35	16.0
72.0	35	18.0

*Before adding lime water.

These experiments on the precipitation of calcium carbonate with lime water agreed in giving an end point which was practically constant, even though the temperature varied considerably. Thus, at 2° C. the end point showed the solution to contain 15.5 parts per million of calcium carbonate; at 20° it was 14.5; and at 35° it was 16. In these experiments the alkalinity nearly always increased slightly, after attaining a minimum value, but this was evidently due to the action of the solution on the glass of the bottle. It is evident from Tables 8 and 9 that the speed of the reaction, after the first hour, was greater at 35° than at 2°. It was noticed that in the experiment where the water was kept at 2° the calcium carbonate did not come down as a colloidal precipitate, but gradually separated from the solution in very fine crystals.

PRECIPITATION OF MAGNESIUM HYDROXIDE WITH LIME.

The experiments on the precipitation of magnesium hydroxide with lime were carried on in the same manner as those for calcium carbonate. Two experiments were made at first, one at 20° C. and one at 37° C. The results of these experiments are given in Tables 10 and 11.

TABLE 10.

Time in Hours	Temperature	Observed Alkalinity	Alkalinity Due to MgO_2H_2
0	22° C.	292*	..
0.25	21	202	..
0.75	21	104	29
9.0	20	62	23
27.0	20	58	37
99.0	20	47	21
195.0	20	32	17
267.0	20	33	17

*Before adding lime water.

TABLE 11.

Time in Hours	Temperature	Observed Alkalinity	Alkalinity Due to MgO_2H_2
0	31° C.	220	..
1.5	31	73	45.0
5.0	34	56	32.0
29.0	37	45.5	27.5
53.0	37	34.5	17.5
101.0	37	29.0	15.0
297.0	37	28.0	15.0

In these experiments the observed alkalinities represent, of course, not only the magnesium hydroxide, but also the calcium carbonate derived from the lime water added. In order to obtain figures for the magnesium hydroxide alone, there were subtracted from the observed alkalinities the amounts of normal calcium carbonate present in solution at corresponding times and temperatures, as shown by those experiments in which $CaCO_3$ alone was precipitated. These results are given in the last columns of these two tables.

It will be seen from these experiments that the reaction with lime water proceeds more rapidly in the case of magnesium bicarbonate than in the case of calcium bicarbonate.

In order to obtain better values for MgO_2H_2, two precipitation experiments were made together, under the same conditions of temperature and time, one with calcium bicarbonate, the other with magnesium bicarbonate, the temperature being about 35° C. The results of this experiment are given in Table 12.

TABLE 12.

TIME IN HOURS	ALKALINITY IN PARTS PER MILLION		
	Calcium Carbonate	Magnesium Hydrate and Calcium Carbonate	Difference (MgO_2H_2)
0.25	55	65	30
0.5	40	66	26
1	33	60	27
2	29	55	26
3	28	53	25
5	25	50	25
10	22	48	26
24	18.5	39	20.5
48	16	36	20

The reason why the magnesium reaction takes place more rapidly than the calcium may be due to the fact that in the former case the precipitate is colloidal in character, while in the latter case it is crystalline, although colloidal for a short time at first. It apparently takes some time for calcium carbonate to precipitate completely in this crystalline form.

These facts have an important bearing upon the practical operation of water-softening plants. Since the reaction of lime water on the bicarbonates of calcium and magnesium is not instantaneous, but requires a certain amount of time for completion, it follows that, in order to obtain the best results, water-softening plants must be designed of such capacity as to give time for this reaction to be pretty well advanced before the water leaves the settling tanks. A study of the practical operation of a number of plants has shown that, where the capacities of the coagulation basins are large, the results are better than where they are small. Thus, at Winnipeg, Manitoba, where the time interval is less than two hours, the resulting alkalinity of the water is 80 parts per million, while at Oberlin, Ohio, where the time interval is more than one day, the resulting alkalinity is sometimes as low as 28 parts per million. In certain plants where the time interval is six hours, the results are intermediate between those mentioned.

It is a well-known fact that in most water-softening plants where recarbonization is not practiced, "after-deposits" of lime are apt to form on the sides of the settling tanks, on the sand grains of the filter, and in the distribution pipes. Analyses of these deposits made by the writers have shown them to be composed almost entirely of calcium carbonate, with almost no magnesium. The reason for this appears to be connected with the fact that the rate of the reaction in the case of calcium is slower than in the case of magnesium, and partly, of course, to the fact that the calcium content of most waters considerably exceeds the magnesium content. In one case recently called to our attention, the sand in the filter had become so encrusted with calcium carbonate that its effective size had increased from .40 to .60 mm. These "after-deposits" may be prevented by resorting to the method of recarbonization, which supplies to the water enough free carbonic acid to redissolve, as bicarbonates, the excess of calcium carbonate, and perhaps magnesium hydroxide, which would otherwise gradually settle out.

SUMMARY AND CONCLUSIONS.

1. The solubility of normal calcium carbonate, as determined by direct experiment, was found to vary from 12 to 14 parts per million; by the precipitation experiments with lime water it was found to be about 14.5 parts per million; but this figure is subject to a subtractive correction on account of the action of the alkaline solution on the glass. The most probable value for the solubility of this salt, at ordinary temperatures, may be taken, therefore, as 13 parts per million.

2. The solubility of magnesium hydrate, as determined by direct experiment, was found to be 12 parts per million. By the precipitation experiments with lime it was found to be 10 parts per million, which is probably more nearly correct, and which may be taken as the most probable value. This is equivalent to an alkalinity of 17 parts per million.

3. The reaction between lime water and calcium bicarbonate requires several days for its completion at ordinary temperatures, but is much more rapid at 37° C. than at the freezing point. The greater part of the precipitate, however, separates within six hours at ordinary temperatures. The longer the period which can be allowed for the reaction, the better, therefore, is the result.

4. The reaction between lime water and magnesium bicarbonate takes place somewhat more rapidly than in the case of calcium. This is apparently due to the fact that the precipitate formed is colloidal instead of crystalline.

The delayed reaction in the case of calcium explains why "after-deposits," so often found in water-softening plants, contain so little magnesium.

5. In order to prevent the formation of "after-deposits" some method of recarbonization is necessary when the time allowed for the reactions is short.

6. The effect of the presence of different salts on the solubility of calcium carbonate and magnesium hydroxide was not determined in these experiments, but left for more complete study.

APPENDIX.

1. A. M. COMEY. *A Dictionary of Chemical Solubilities*, 1896.

2. CHEVALET. *Ztschr. f. anal. Chem.*, 1869, 8, p. 91.

200 c.c. of $CaCO_3$ solution were distilled with five grains NH_4Cl. The first 100 c.c. of the distillate were passed into 10 c.c. dilute H_2SO_4. The CO_2 was boiled off and the still uncombined acid determined volumetrically. No details are given as to method of making $CaCO_3$ solution.

3. HOFFMANN. *Ztschr. f. anal. Chem.*, 1865, 4, p. 414.

A solution of calcium bicarbonate was subjected to prolonged boiling and the filtrate analyzed. It is not stated whether the boiling was conducted in glass, porcelain or platinum.

4. PELIGOT, mentioned by Bineau (*vide sq.*) as having obtained a value of 20 parts per million. No reference given.

5. WELTZIEN. *Ann. d. Chem. u. Pharm.*, 1865, 136, p. 165. No particulars of method given.

6. BINEAU. *Ann. de chim. et phys.*, Par., 1857 (3), 51, p. 290.

Solutions of $CaCO_3$ were obtained, (1) by shaking an excess of $CaCO_3$ with pure water, (2) by adding a slight excess of calcium salt to dilute solution of Na_2CO_3, and (3) by prolonged boiling of calcium bicarbonate solution. The amount of $CaCO_3$ in solution was determined by the addition of an excess of dilute H_2SO_4, expelling CO_2 by heat or in a partial vacuum, and titrating back with standardized lime water. Special precautions were taken against the action of the CO_2 of the atmosphere, and the action of $CaCO_3$ solution on glass. "The result in which the author places most confidence is 16 parts per million and the solubility of $CaCO_3$ is certainly not more than 20 parts per million." These experiments were evidently made with great care.

7. SCHLÖSING. *Compt. rend. Acad. d. Sc.*, Par., 1872, 74, 1552.

"The solubility of normal $CaCO_3$ in pure water was determined, with all necessary precautions, at 16° C."

8. HOLLEMAN. *Ztschr. f. physik. Chem.*, 1893, 12, 125.

Carefully prepared $CaCO_3$ was agitated with water of great purity in small vessels, protected from the CO_2 of the air by tubes of soda lime. The electrical conductivity of the solution thus obtained was carefully measured, and the amount of salt in solution calculated from this figure. The method was first checked by solutions of known composition, and found to be accurate within about 1 per cent, the greatest deviation being 2.8 per cent.

9. KOHLRAUSCH AND ROSE. *Ztschr. f. physik. Chem.*, 1893, 12, p. 241.

Pure $CaCO_3$ was added to water of great purity, in flasks, well shaken, and the electrical conductivity determined until it reached a constant value, from which the solubility of $CaCO_3$ could be calculated. The solution was protected from the CO_2 of the air and special attention was paid to the quality of the glass used. An exactly similar method was used to determine the solubility of MgO_2H_2.

. . . . Kohlrausch and Rose adduce the following advantages for the electrical conductivity method of determining solubilities, which they claim is the best method for this purpose, when the values to be determined are small:

The progress of solution can be followed, and when a constant value is attained, the fact is immediately recognized.

There is no necessity for separating from the solution the excess of undissolved substance, since the latter introduces no perceptible error in the determination. Hence, filtration as well as evaporation and other lengthy operations, which involve the possible introduction of impurities, are avoided, and the substance can be used in as finely divided condition as may be desired.

Only a small amount of substance is required; the determination requires but a short time, thus avoiding errors introduced by the action of the solvent upon the containing vessel.

The determination is conducted in closed vessels, thus avoiding the influence of foreign matter, for instance, the CO_2 of the air.

10. KIMBERLY. *Jour. Inject. Dis.*, 1905, Supplm. No. 1., p. 157.

11. FRESENIUS. *Ann. d. Chem. u. Pharm.*, 1847, 59, p. 117.

Carefully purified MgO was digested with pure cold water, filtered, and the filtrate evaporated to dryness in platinum dish. No mention is made of precautions taken against action of CO_2 of the air or the action of MgO_2H_2 solution on glass.

12. BINEAU. *Compt. rend. Acad. d. Sc.*, Par., 1855, 41, 510.

Method not given. Author states that solubility is much increased by action of CO_2 of air.